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DETERMINATION OF VOLATILE PESTICIDES IN INDUSTRIAL AND MUNICIPAL WASTEWATERS

by

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16. ABSTRACT

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The final method was applied to two representative wastewaters spiked at appropriate levels in order to determine precision and accuracy of the method. For a wastewater sample spiked with 5 µg/L of chloropicrin and ethylene dibromide, the recoveries were 98 ± 12 percent and 69 ± 6.7 percent, respectively. For a wastewater spiked at 50 µg/L of chloropicrin and ethylene dibromide, the recoveries were 98 ± 3.3 percent and 108 ± 4.8 percent, respectively. Method detection limits (MDLs) for the two compounds in distilled water were 0.84 µg/L for chloropicrin and 0.20 µg/L for ethylene dibromide. MDLs in wastewaters may be higher due to interfering compounds.

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati, conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid wastes.

- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.

- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

This report is one of a series that investigates the analytical behavior of selected pesticides and suggests a suitable test procedure for their measurement in wastewater. The method was modeled after existing EPA methods being specific yet as simplified as possible.

Robert L. Booth

Robert L. Booth, Acting Director
Environmental Monitoring and Support
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ABSTRACT

A method was developed for the determination of two volatile pesticides, chloropicrin and ethylene dibromide, in wastewaters. The methods development program consisted of a literature review; determination of the extraction efficiency for each compound from water into cyclohexane; and determination of suitable gas chromatographic analysis conditions.

In order to determine precision and accuracy, the final method was applied to two representative wastewaters spiked at appropriate levels. For a wastewater sample spiked with 5 µg/L of chloropicrin and ethylene dibromide, the recoveries were 98 ± 12 percent and 69 ± 6.7 percent, respectively. For a wastewater spiked at 50 µg/L of chloropicrin and ethylene dibromide, the recoveries were 98 ± 3.3 percent and 108 ± 4.8 percent, respectively. Method detection limits (MDLs) for the two compounds in distilled water were 0.84 µg/L for chloropicrin and 0.20 µg/L for ethylene dibromide. The MDLs in wastewaters may be higher due to interfering compounds.

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SECTION 1

INTRODUCTION

Chloropicrin and ethylene dibromide are insecticides used for fumigation of soils and stored grains. The CAS registry number for chloropicrin is 76-06-02, and its IUPAC name is trichloronitromethane. Its common synonyms include "Bromofume", "Dowfume N-8", "Iscobrome D", "Soilfume", Aadibroom", "Dowfume W 85", "Nefis", "Sanhyum". The CAS registry number for ethylene dibromide is 106-93-4, and its IUPAC name is 1,2-dibromomethane. Its common synonyms include "Acquinite", "Larvacide", "Microlysin", and "Picfume".

Chloropicrin is produced by the action of hypochlorites on nitromethane to give a colorless liquid with a molecular weight of 161.4 and a boiling point of 112.4°C. The compound decomposes violently at high temperatures. It is nonflammable and chemically inert; its solubility at 0°C is 2.27 g/L of water. Chloropicrin is a lachrymator and has an LD50 of 250 mg/kg in rats. A literature survey provided a gas chromatographic (GC) analysis method using 2% OV-101 and a thermal conductivity detector and a purge and trap gas chromaographic-mass spectrometric (GC-MS) procedure using a Tenax GC trap and a Tenax GC column (1). Some electron impact-mass spectrometry information was found (2). Extraction solvents described included hexane, ethyl ether, and pentane (3). A spectrophotometric method has also been used to analyze for this compound (4).

Ethylene dibromide is produced by the bromination of ethane to give a colorless liquid with a molecular weight of 187.9 and a boiling point of 131.5°C. It is stable and nonflammable and has a solubility at 30°C of 4.3 g/L of water. The LD50 for this compound is 117-146 mg/kg in rats. Dermal applications will cause severe burning. A literature survey provided several extraction solvents: ethyl acetate (5), hexane (6), and benzene (7). Various analytical methods such as sweep co-distillation, and steam distillation, were used (8). Gas chromatography-electron capture detector (GC-ECD) analysis methods were described using a 15% Ucon oil LB-550-X column (5, 9), a 30% DC-200 column (8), and columns of 5% didecyl phthalate, 5% Carbowax 20M-TPA, and 3% OV-225 (6). Ethylene dibromide has been reacted with alkali and the resultant bromide ion was determined by Volhard titration (7).

Because of the volatilities and solubilities of these compounds, the selected approach for solvent extraction was similar to that currently being used by the EPA for determining trihalomethanes in drinking water (10). Minimum mdifications were required.

SECTION 2

CONCLUSIONS

Chloropicrin and ethylene dibromide are volatile compounds and are not amenable to standard Kuderna-Danish (K-D) concentration procedures. For this reason no concentration methods were developed. Since adsorption column cleanup procedures would involve dilution of the sample, this step was also eliminated. The final method is included as Appendix A of this report.

EXTRACTION

A modified version of the EPA Method 501.2 for trihalomethanes in drinking water gives acceptable results for these compounds and is familiar to other laboratories. It is, therefore, the extraction method of choice for chloropicrin and ethylene dibromide.

CHROMATOGRAPHY

Good separation and quantification can be achieved by using GC-ECD and either of two columns: 1% SP-1000 on Carbopak B or 30% OV-17 on Gas Chrom Q. Since the 1% SP-1000 on Carbopak B column is already used for two US EPA methods, 601 and 624, this was chosen as the primary column for the analysis of these compounds. The 30% OV-17 was presented in the method as a secondary column.

VALIDATION STUDIES

The MDLs for both compounds were at or below the required 1 µg/L level. Analytical curves were constructed for each compound from 10-1000 µg/L; these were linear over the entire range. Recovery studies were performed on two relevant wastewaters: one with a high-level background and one with a low-level background. Neither of the compounds of interest was detected in these waters. Satisfactory recoveries from both low and high level spikes of the chloropicrin and from the high level spikes of the ethylene dibromide were achieved. Recoveries from the low level spike of the ethylene dibromide were less than 85 percent, presumably due to some chemical characteristic of the wastewater used.

SECTION 3

EXPERIMENTAL

Since chloropicrin and ethylene dibromide are volatile compounds, K-D concentration and adsorption chromatography cleanup procedures were not developed. Literature surveys indicated that both compounds are stable in water, so stability studies were not performed.

EXTRACTION

The extraction procedure employed was similar to the US EPA Method 501.2 for the determination of trihalomethanes in drinking water. The sample was poured into a 40-mL centrifuge tube equipped with a Teflon-lined screw cap to a predetermined 20-mL mark, and its pH adjusted to 6-8 by addition of 6N sodium hydroxide or 6N sulfuric acid. Then four mL of cyclohexane was measured with a four-mL graduated pipette and added to the centrifuge tube. The tube was shaken vigorously for one minute, and the layers were allowed to separate for at least 10 minutes. Centrifugation was sometimes necessary to facilitate phase separation. An aliquot of the cyclohexane layer was withdrawn and analyzed by GC-ECD. Recovery studies were performed by spiking the reagent water with the analytes over a range of concentrations, in triplicate at each level, and determining the percent recovery.

CHROMATOGRAPHY

Five different packed columns were evaluated: 1% SP-2100 on 100/120 mesh Supelcoport, 1% SP-1240 DA on 100/120 mesh Supelcoport, 3% OV-17 on 100/120 mesh Gas Chrom Q, 30% OV-17 on 100/120 mesh Gas Chrom Q, and 1% SP-1000 on Carbopak B.

VALIDATION STUDIES

The MDL for both compounds was determined by spiking them into reagent water at a concentration two times the estimated detection limit of 1 µg/L in water. Seven replicate extractions at analyte concentration of 2 µg/L in water were performed. The amount recovered was determined by external standard calibration, and from these data the MDL was calculated.

An analytical curve was generated to determine the linearity of recovery of the fumigants from reagent water. Reagent water was spiked in duplicate to give analyte concentrations of 10, 50, 100, 500, and 1000 µg/L in water. The water was extracted and plots were constructed of amount recovered vs. amount spiked.

Recovery studies from two relevant wastewaters were also performed. Two wastewaters were analyzed; one was a deep well injection brine from a plant that manufactures ethylene dibromide, and the other was an untreated effluent from a plant that manufactures chloropicrin. The wastewaters were extracted unspiked; seven replicate extractions were performed for each wastewater. It was determined that the brine from the ethylene dibromide manufacturing plant exhibited the higher background and was therefore designated a high-level wastewater. The effluent from the chloropicrin manufacturing plant was designated a low-level wastewater. None of the extracts showed peaks at the retention times for chloropicrin or ethylene dibromide.

Recovery studies were performed by spiking the low-level wastewater at analyte concentrations of 5 µg/L and the high-level wastewater at analyte concentrations of 50 µg/L. Seven replicate extractions were performed for each spiked wastewater.

SECTION 4

RESULTS AND DISCUSSION

EXTRACTION

The extraction solvent used in the method development and validation was cyclohexane. Other solvents such as hexane, heptane, or isooctane can also be used. However, many lots of solvents contain electron-capturing interferences. For this reason, a solvent lot must be analyzed by GC-ECD prior to use to determine its suitability for use with this method.

Recoveries of analytes spiked into reagent water are presented in Table 1. The recoveries were all very good except at the lower concentration levels (one to two µg/L), and these recoveries were within the acceptable range. The relative standard deviations were always less than 10 percent.

TABLE 1. RECOVERY OF FUMIGANTS FROM WATER

	Chloropicrin		Ethylene Dibromide	
Spike Level, µg/L	Average Recovery, %(a)	Relative Standard Deviation, %	Average Recovery, %(a)	Relative Standard Deviation, %
1000	109	4.7	97	3.7
100	98	0.6	96	1.6
40	95	3.1	100	2.8
20	90	2.3	95	3.2
10	90	2.6	100	4.7
4	85	3.5	100	5.7
2	80	5.1	95	4.8
1	78	7.7	84	10

(a) Average of triplicate analyses.

CHROMATOGRAPHY

Of the five columns evaluated, three (1% SP-2100, 1% SP-1240 DA and 3% OV-17) were unacceptable. The chloropicrin and ethylene dibromide were not well resolved from the solvent front and peak shapes were not acceptable. The 30% OV-17 and 1% SP-1000 columns both gave good peak shapes and good resolution even at low concentration levels. The 1% SP-1000 column is already used for two US EPA Methods, 601 and 624. For these reasons, the 1% SP-1000 column was chosen as the primary column and used for method validation. The 30% OV-17 column was chosen as the secondary column.

The retention times for chloropicrin and ethylene dibromide on the primary column (1% SP-1000 on Carbopak B) were 5.6 minutes and 9.9 minutes respectively. The retention times on the secondary column (30% OV-17) were 2.25 minutes for chloropicrin and 3.3 minutes for ethylene dibromide. Chromatograms of standard solutions of the two compounds on each column are presented in Figures 1 and 2 respectively. The extraneous peaks present are electron-capturing contaminants in the cyclohexane used to prepare the standards.

The specific GC conditions used were:

Gas Chromatograph:	Varian Model 3700
Detector:	Electron capture,
Temperature Injector:	200°C
Detector Temperature:	320°C
Column Temperature:	135°C (SP-1000), 80°C (OV-17); isothermal
Carrier Gas:	Nitrogen with flow rate of 30 mL/min.

VALIDATION STUDIES

The MDLs for chloropicrin and ethylene dibromide were determined to be 0.84 µg/L and 0.20 µg/L respectively. For any further validations based on the MDLs a "working" value of 1 ppb was used for both compounds. Data from the MDL determination are presented in Table 2.

TABLE 2. DATA FROM MDL DETERMINATIONS

Compound	Spike Level, µg/L	Amount Recovered, µg/L(a)	Standard Deviation	MDL
Chloropicrin	2.00	2.46	0.27	0.84
Ethylene Dibromide	2.00	1.92	0.06	0.20

(a) Average of seven analyses.

The analytical curves (amount recovered vs. amount spiked) generated are presented in Figures 3 and 4. The recoveries were close to linear over the concentration range of 10-1000 µg/L. Data used to generate these plots are in Table 3.

TABLE 3. DATA FROM GENERATION OF ANALYTICAL CURVE

Amount Spiked, µg/L	Amount Recovered, µg/L(a)	
	Chloropicrin	Ethylene Dibromide
10	9.90	9.40
50	48.5	53.4
100	92.0	101
500	555	507
1000	975	985

(a) Average of duplicate analyses.

Chromatograms of extracts of the unspiked and spiked wastewaters are presented in Figures 5, 6. The average percent recoveries and the relative standard deviations for the spiked extractions are presented in Table 4. Recoveries were acceptable for the high and low level spikes of chloropicrin and for the high level spike of ethyene dibromide. The recovery of ethylene dibromide at the low spike level five µg/L was below 85 percent. Since recoveries of greater than 85 percent were achieved from distilled water at concentrations lower than five µg/L, this poor recovery may be due to some characteristic of the wastewater used for the low level spike study.

TABLE 4. RECOVERY OF CHLOROPICRIN AND ETHYLENE DIBROMIDE FROM WASTEWATERS

Spike Level, µg/l	Chloropicrin		Ethylene Dibromide	
	Average Recovery, %(a)	Relative Standard Deviation, %	Average Recovery, %(a)	Relative Standard Deviation, %
5	98	11.6	69	6.7
50	98.1	3.3	108	4.8

(a) Average of seven analyses.

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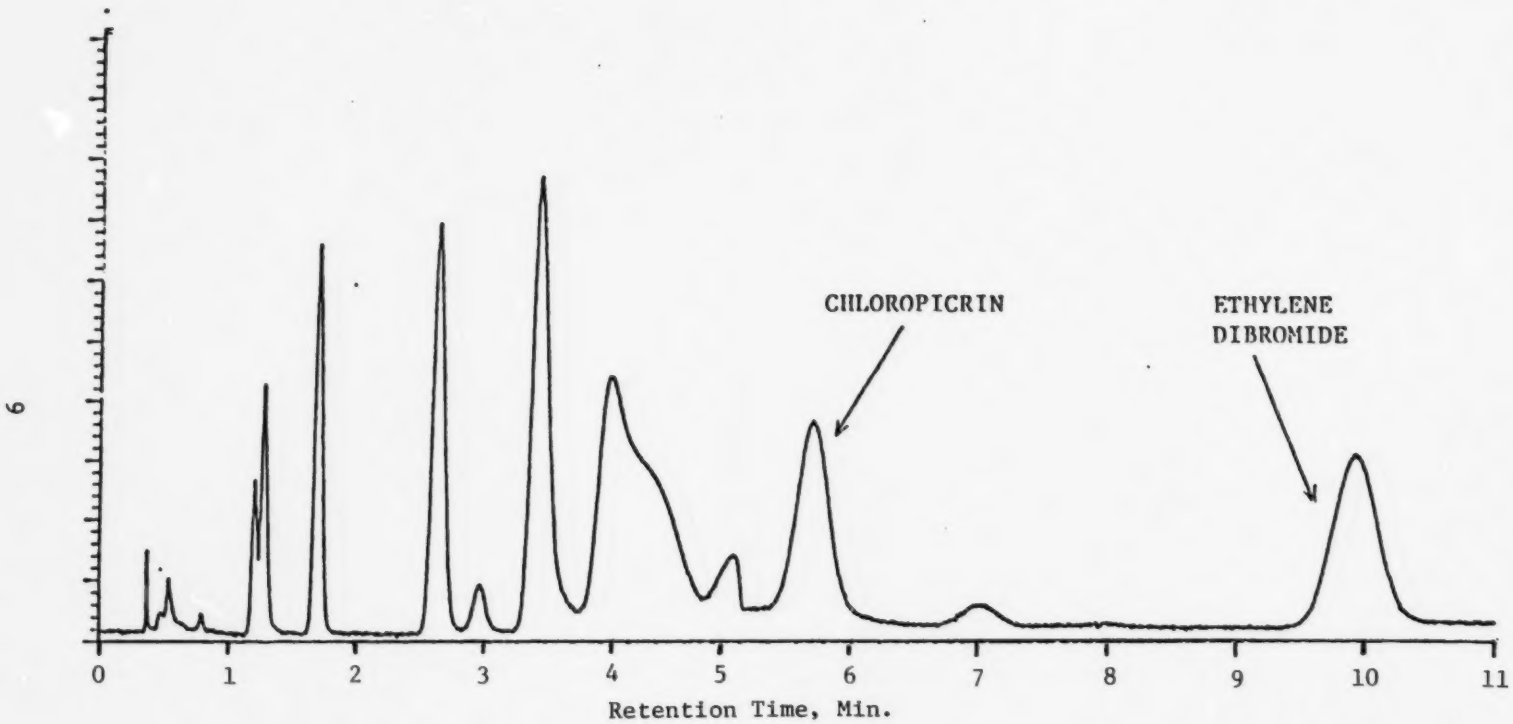

Figure 1. GC-ECD Chromatogram of 200 ng Chloropicrin and Ethylene Dibromide (Column 1).

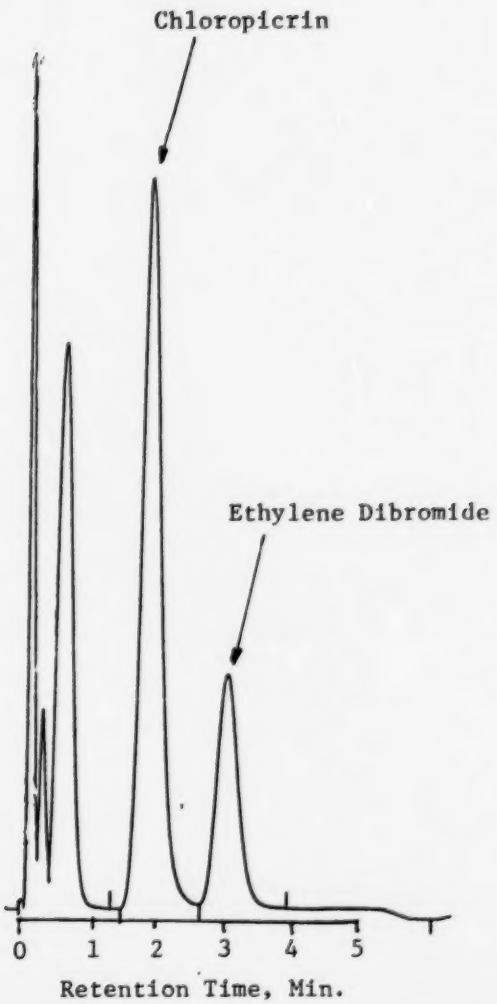

Figure 2. GC-ECD Chromatogram of 400 ng Chloropicrin and Ethylene Dibromide (Column 2).

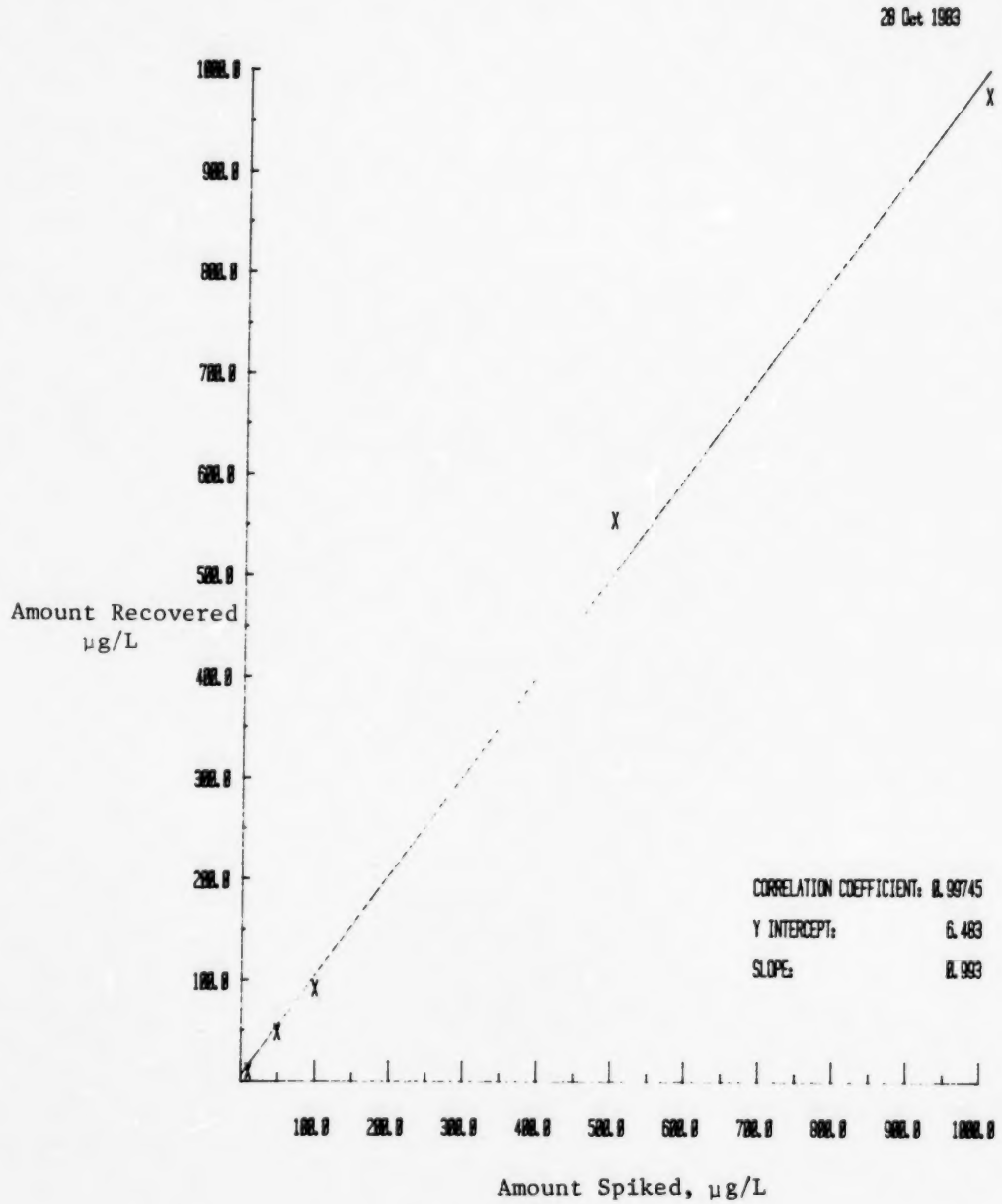

Figure 3. Analytical Curve for Chloropicrin.

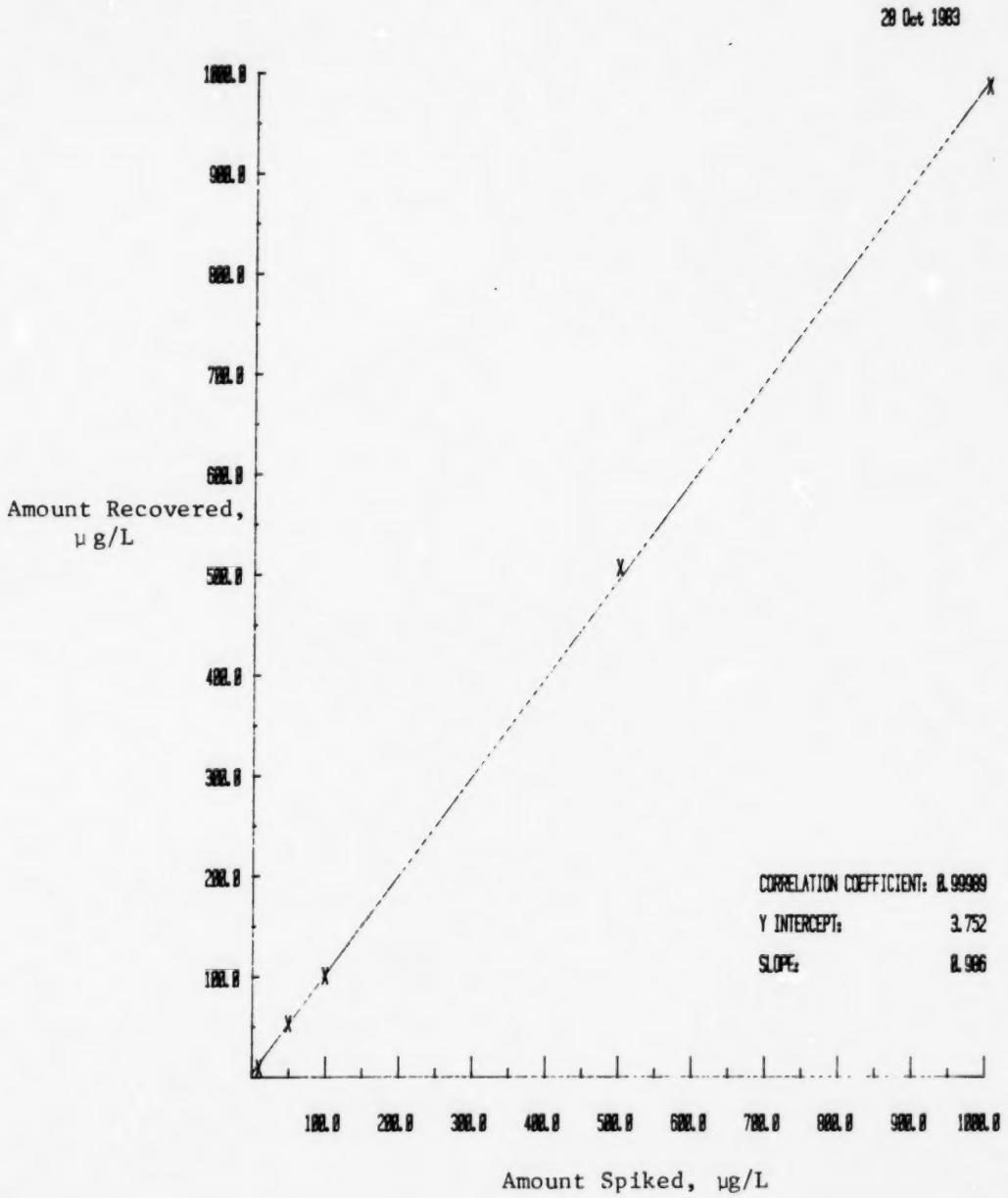

Figure 4. Analytical Curve for Ethylene Dibromide.

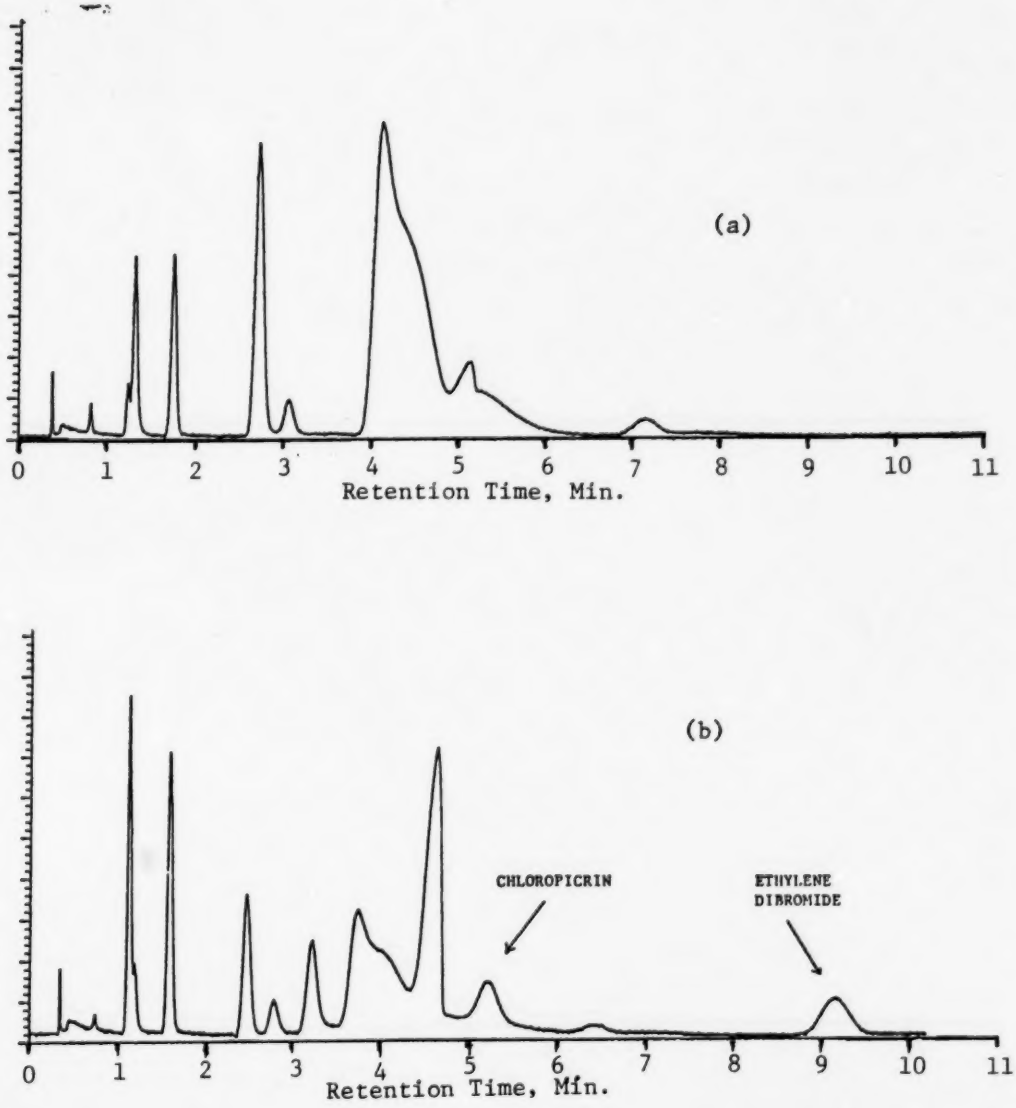

Figure 5. GC-ECD Chromatogram of Cyclohexane Extract of Low Level Wastewater (a) Unspiked and (b) Spiked With 5 µg/L of Chloropicrin and Ethylene Dibromide.

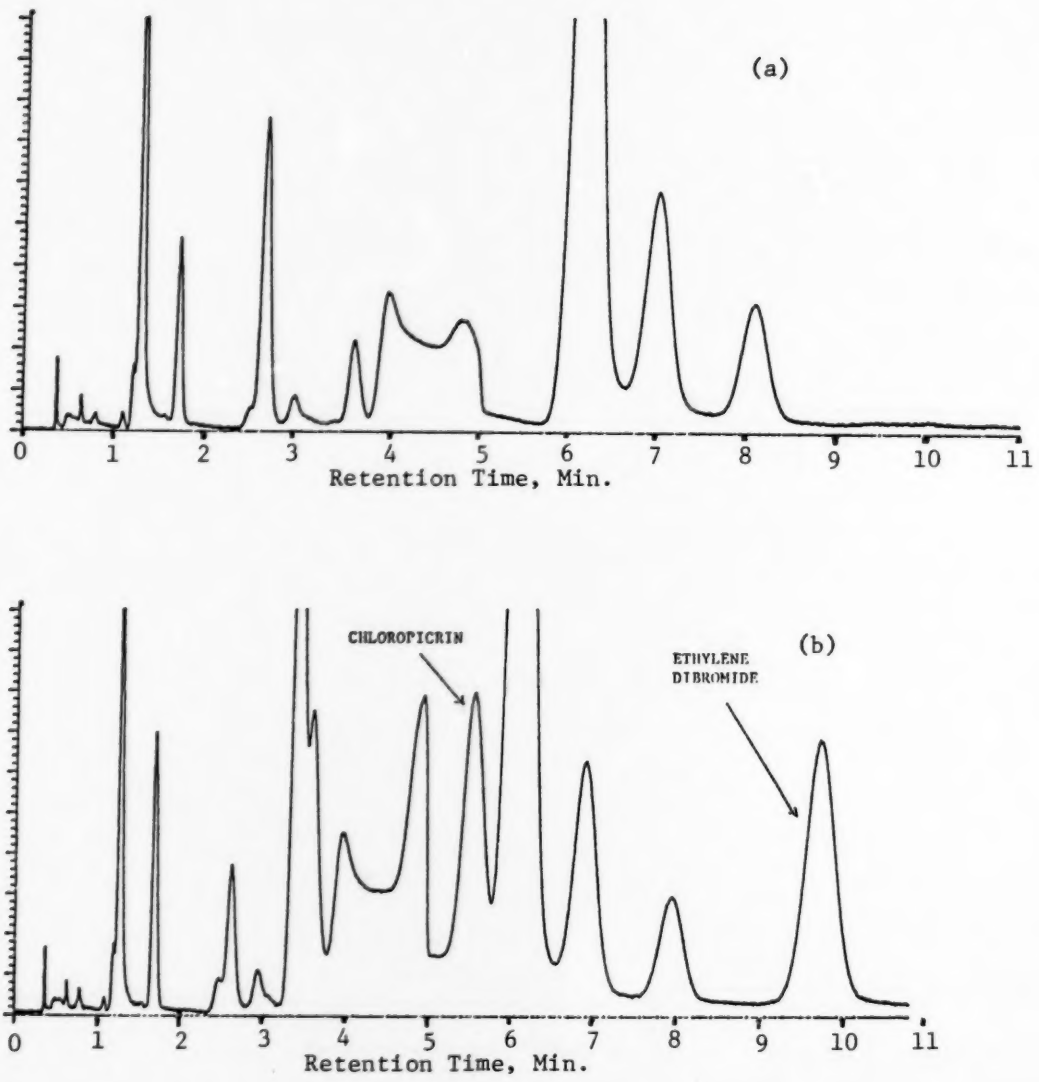

Figure 6. GC-ECD Chromatogram of Cyclohexane Extract of High Level Wastewater (a) Unspiked and (b) Spiked With 50 µg/L of Chloropicrin and Ethylene Dibromide.

METHOD 618 DETERMINATION OF VOLATILE PESTICIDES IN MUNICIPAL AND INDUSTRIAL WASTEWATERS BY GAS CHROMATOGRAPHY

1. Scope and Application

1.1 This method covers the determination of certain volatile pesticides. The following parameters can be determined by this method:

Parameter	CAS No.
Chloropicrin	76-06-2
Ethylene dibromide	106-93-4

1.2 This is a gas chromatogrpahic (GC) method applicable to the determination of the compounds listed above in municipal and industrial discharges.

1.3 The method detection limit (MDL, defined in Section 15) for each compound is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.4 **This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.**

1.5 When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Section 14 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

2. Summary of Method

2.1 A measured volume of sample, 20 mL, is extracted with cyclohexane. The cyclohexane extract is analyzed with no additional treatment. Gas chromatographic conditions are described which permit the separation of the compounds in the extract and their measurement by an electron capture detector.

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or elevated baselines in gas chromatograms. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.5.

3.1.1 Glassware must be scrupulously cleaned.[1] Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent and thorough rinsing with tap and reagent water. Drain dry, and heat in an oven or muffle furnace at 400°C for 15 to 30 min. Do not heat volumetric ware. Thorough rinsing with acetone may be substituted for the heating. After drying and cooling, seal and store glassware in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. Some samples may require a clean-up approach to achieve the MDL listed in Table 1.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard.

Chloropicrin produces severe sensory irritation in upper respiratory passages. It has strong lacrimatory properties and produces increased sensitivity after frequent exposures. Taken orally, chloropicrin causes severe nausea, vomiting, colic, and diarrhea. Chloropicrin is a potent skin irritant. Ethylene dibromide liquid on the skin causes blisters if evaporation is delayed. Inhalation of ethylene dibromide causes delayed pulmonary lesions. Prolonged exposure may also result in liver and kidney injury. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified[2-4] for the information of the analyst.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete sampling.

5.1.1 Vial - 25-mL capacity or larger, equipped with a screw cap with hole in center (Pierce No. 13075 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105°C before use.

5.1.2 Septum - Teflon-faced silicone (Pierce No. 12722 or

equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105°C before use.

5.2 Glassware (All specifications are suggested).

5.2.1 Centrifuge tube - 40 mL, with screw cap lined with Teflon.

5.2.2 Pipette - 4 mL graduated.

5.2.3 Graduated cylinder - 25 mL.

5.2.4 Volumetric flask -10 mL, ground glass stoppered.

5.3 Balance - Analytical, capable of accurately weighing to the nearest 0.0001 g.

5.4 Gas chromatograph - Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

5.4.1 Column 1 - 180 cm long x 2 mm ID glass, packed with 1% SP-1000 on Carbopak B (60/80 mesh) or equivalent. This column was used to develop the method performance statements in Section 15. Alternative columns may be used in accordance with the provisions described in Section 11.1.

5.4.2 Column 2 - 180 cm long x 2 mm ID glass, packed with 30% OV-17 on Gas Chrom Q (100/120 mesh) or equivalent.

5.4.3 Detector - electron capture. This detector has proven effective in the analysis of wastewaters for the compounds listed in the scope and was used to develop the method performance statements in Section 15. Alternative detectors, including a mass spectrometer, may be used in accordance with the provisions described in Section 12.1.

6. Reagents

6.1 Reagent water - Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each compound of interest.

6.2 Cyclohexane - pesticide quality or equivalent. Because of the frequent occurrence of electron-capturing contaminants in solvents, several lots of solvent, or a different solvent, e.g. hexane, heptane, or isooctane, may have to be analyzed to find a suitable extraction solvent.

6.3 Sodium hydroxide - 6N in distilled water.

6.4 Sulfuric acid - 6N in distilled water.

6.5 Stock standard solutions (20 mg/mL) - Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions. Prepare stock solutions in cyclohexane using assayed liquids.

6.5.1 Place about 9.5 mL of pesticide-quality cyclohexane in a 10-mL volumetric flask. Allow the flask to stand, unstoppered, for about 5 minutes or until all cyclohexane wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg. Using a 250-µL syringe, immediately add 121 µL of chloropicrin (d_4^{20} = 1.66) and/or 92 µL of ethylene dibromide (d_4^{20} = 2.18). The liquid must fall directly into the cyclohexane without contacting the neck of the flask. Reweigh, dilute to volume, stopper, and mix by inverting the flask several times. Calculate the concentration in milligrams per milliliter (mg/mL)

from the net gain in weight. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

6.5.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Frequently check stock standard solutions for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.5.3 Stock standard solutions must be replaced after six months or sooner if comparison with check standards indicates a problem.

7. Calibration

7.1 Establish gas chromatographic operating parameters equivalent to those indicated in Table 1. The gas chromatographic system may be calibrated using either the external standard technique (Section 7.2) or the internal standard technique (Section 7.3).

7.2 External standard calibration procedure:

7.2.1 For each compound of interest, prepare calibration standards at a minimum of three concentration levels by adding accurately measured volumes of one or more stock standards to a volumetric flask and diluting to volume

with cyclohexane. One of the external standards should be representative of a concentration near, but above, the method detection limit. The other concentrations should correspond to the range of concentrations expected in the sample concentrates or should define the working range of the detector.

7.2.2 Using injections of 1 to 5 µL of each calibration standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each parameter. Alternatively, the ratio of the response to the mass injected, defined as the calibration factor (CF), can be calculated for each compound at each standard concentration. If the relative standard deviation of the calibration factor is less than 10% over the working range, the average calibration factor can be used in place of a calibration curve.

7.2.3 The working calibration curve or calibration factor must be verified on each working shift by the measurement of one or more calibration standards. If the response for any compound varies from the predicted response by more than $\pm$ 10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that parameter.

7.3 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be specified; however, bromoform has been shown to be satisfactory in some cases.

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each compound of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with cyclohexane. One of the standards should be representative of a concentration near, but above, the method detection limit. The other concentrations should correspond to the range of concentrations expected in the sample concentrates or should define the working range of the detector.

7.3.2 Using injections of 1 to 5 µL of each calibration standard, tabulate the peak height or area responses against the concentration for each compound and internal standard. Calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is})/(A_{is} C_s)$$

where:

A_s = Response for the compound to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard in µg/L.

C_s = Concentration of the compound to be measured in µg/L.

If the RF value over the working range is constant, less than 10% relative standard deviation, the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} against RF.

7.3.3 The working calibration curve or RF must be verified on each working shift by the measurement of one or more calibration standards. If the response for any compound varies from the predicted response by more than $\pm$ 10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be preparedfor that compound.

7.4 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

8. Quality Control

8.1 Each laboratory using this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 The laboratory must spike and analyze a minimum of 10% of all samples to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 Select a representative spike concentration for each compound to be measured. Using stock standards, prepare a

quality control check sample concentrate in methanol such that a 4-µL aliquot of the check sample concentrate in 20-mL of water gives the selected concentration.

8.2.2 Using a 10-µL syringe add 4 µL of the check sample concentrate to each of a minimum of four 20-mL aliquots of reagent water. A representative wastewater may be used in place of the reagent water, but one or more additional aliquots must be analyzed to determine background levels, and the spike level must exceed twice the background level for the test to be valid. Analyze the aliquots according to the method beginning in Section 10.

8.2.3 Calculate the average percent recovery (R), and the standard deviation of the percent recovery (s), for the results. Wastewater background corrections must be made before R and s calculations are performed.

8.2.4 Using the appropriate data from Table 2, determine the recovery and single operator precision expected for the method, and compare these results to the values measured in Section 8.2.3. If the data are not comparable, review potential problem areas and repeat the test.

8.3 The analyst must calculate method performance criteria and define the performance of the laboratory for each spike concentration and compound being measured.

8.3.1 Calculate upper and lower control limits for method performance as follows:

Upper Control Limit (UCL) = R + 3 s

Lower Control Limit (LCL) = R - 3 s

where R and s are calculated as in Section 8.2.3. The UCL and LCL can be used to construct control charts[5] that are useful in observing trends in performance.

8.3.2 The laboratory must develop and maintain separate accuracy statements of laboratory performance for wastewater samples. An accuracy statement for the method is defined as R $\pm$ s. The accuracy statement should be developed by the analysis of four aliquots of wastewater as described in Section 8.2.2, followed by the calculation of R and s. Alternately, the analyst may use four wastewater data points gathered through the requirement for continuing quality control in Section 8.4. The accuracy statements should be updated regularly.[5]

8.4 The laboratory is required to collect in duplicate a portion of their samples to monitor spike recoveries. The frequency of spiked sample analysis must be at least 10% of all samples or one sample per month, whichever is greater. One aliquot of the sample must be spiked and analyzed as described in Section 8.2. If the recovery for a particular compound does not fall within the control limits for method performance, the results reported for that compound in all samples processed as part of the same set

must be qualified as described in Section 13.3. The laboratory should monitor the frequency of data so qualified to ensure that it remains at or below 5%.

8.5 Before processing any samples, the analyst should demonstrate through the analysis of a 20-mL aliquot of reagent water that all glassware and reagents interferences are under control. Each time a set of samples is extracted or there is a change in reagents, a laboratory reagent blank should be processed as a safeguard against laboratory contamination.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should perform analysis of quality control materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers having a total volume of at least 25 mL. Fill the sample bottle just to overflowing in such a manner that no air bubbles pass through the

sample as the bottle is being filled. Seal the bottle so that no air bubbles are entrapped in it. Store the sample in an inverted position and maintain the hermetic seal on the sample bottle until the time of analysis.

9.2 The samples must be iced or refrigerated at 4°C from the time of collection until extraction.

10. Sample Extraction

10.1 Measure 20 mL of sample by pouring the sample into a 40-mL centrifuge tube equipped with a Teflon-lined screw cap to a predetermined 20-mL mark. Adjust pH of sample to 6-8 by addition of 6N sodium hydroxide or 6N sulfuric acid. Measure 4.0 mL of extraction solvent with a 4-mL graduated pipette and add to the centrifuge tube.

10.2 Shake the tube vigorously for one minute. Allow the layers to separate for at least 10 minutes. Centrifuge, if necessary, to facilitate phase separation.

10.3 Withdraw an aliquot of the solvent layer and proceed with gas chromatographic analysis.

11. Cleanup and Separation

11.1 Cleanup procedures are not generally necessary. If particular circumstances demand the use of a cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of each compound of interest is no less than 85%.

12. Gas Chromatography

12.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are estimated retention times and method detection limits that can be achieved by this method. Examples of the separations achieved by Columns 1 and 2 are shown in Figures 1 and 2, respectively. Other packed columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met. Capillary (open-tubular) columns may also be used if the relative standard deviations of responses for replicate injections are demonstrated to be less than 6% and the requirements of Section 8.2 are met.

12.2 Calibrate the system daily as described in Section 7.

12.3 If the internal standard approach is being used, the analyst must not add the internal standard to sample extracts until immediately before injection into the instrument. Mix thoroughly.

12.4 Inject 1 to 5 µL of the sample extract using the solvent-flush technique.[6] Record the volume injected to the nearest 0.05 µL, and the resulting peak size in area or peak height units. An automated system that consistently injects a constant volume of extract may also be used.

12.5 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the

standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

12.6 If the response for the peak exceeds the working range of the system, dilute the extract and reanalyze.

12.7 If the measurement of the peak response is prevented by the presence of interferences, further cleanup is required.

13. Calculations

13.1 Determine the concentration of individual compounds in the sample.

13.1.1 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor in Section 7.2.2. The concentration in the sample can be calculated as follows:

$$\text{Concentration, } \mu g/L = \frac{(A)(V_t)}{(V_i)(V_s)}$$

where:

A = Amount of material injected, in nanograms.

V_i = Volume of extract injected in µL.

V_t = Volume of total extract in µL.

V_s = Volume of water extracted in mL.

13.1.2 If the internal standard calibration procedure is used, calculate the concentration in the sample using the

response factor (RF) determined in Section 7.3.2 as follows:

$$\text{Concentration, } \mu g/L = \frac{(A_s)(I_s)}{(A_{is})(RF)(V_o)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

I_s = Amount of internal standard added to each extract in µg.

V_o = Volume of water extracted, in liters.

13.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

13.3 For samples processed as part of a set where the laboratory spiked sample recovery falls outside of the control limits in Section 8.3, data for the affected compounds must be labeled as suspect.

14. GC/MS Confirmation

14.1 It is recommended that GC/MS techniques be judiciously employed to support qualitative identifications made with this method. The mass spectrometer should be capable of scanning the mass range from 35 amu to a mass 50 amu above the molecular weight of the compound. The instrument must be capable of scanning the mass range at a rate to produce at least 5 scans per peak but not to

exceed 7 seconds per scan utilizing a 70 V (nominal) electron energy in the electron impact ionization mode. A GC to MS interface constructed of all-glass or glass-lined materials is recommended. A computer system should be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program.

14.2 Gas chromatographic columns and conditions should be selected for optimum separation and performance. The conditions selected must be compatible with standard GC/MS operating practices. Chromatographic tailing factors of less than 5.0 must be achieved.[9]

14.3 At the beginning of each day that confirmatory analyses are to be performed, the GC/MS system must be checked to see that all decafluorotriphenyl phosphine (DFTPP) performance criteria are achieved.[7]

14.4 To confirm an identification of a compound, the background corrected mass spectrum of the compound must be obtained from the sample extract and compared with a mass spectrum from a stock or calibration standard analyzed under the same chromatographic conditions. It is recommended that at least 25 nanograms of material be injected into the GC/MS. The criteria below must be met for qualitative confirmation.

14.4.1 All ions that are present above 10% relative abundance in the mass spectrum of the standard must be present in the mass spectrum of the sample with agreement to plus or minus 10%. For example, if the relative abundance of an ion is 30% in the mass spectrum of the standard, the allowable limits for the relative abundance of that ion in the mass spectrum for the sample would be 20 to 40%.

14.4.2 The retention time of the compound in the sample must be within 6 seconds of the same compound in the standard solution.

14.4.3 Compounds that have very similar mass spectra can be explicitly identified by GC/MS only on the basis of retention time data.

14.5 Where available, chemical ionization mass spectra may be employed to aid in the qualitative identification process.

14.6 Should these MS procedures fail to provide satisfactory results, additional steps may be taken before reanalysis. These may include the use of alternate packed or capillary GC columns or additional cleanup (Section 11).

15. Method Performance

15.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported

with 99% confidence that the value is above zero.[10] The MDL concentrations listed in Table 1 were obtained using reagent water.[8] Similar results were achieved using representative wastewaters.

15.2 This method has been tested for linearity of recovery from spiked reagent water and has been demonstrated to be applicable over the concentration range from 10 x MDL to 1000 x MDL.

15.3 In a single laboratory, Battelle Columbus Laboratories, using spiked wastewater samples, the average recoveries presented in Table 2 were obtained. Seven replicates each of two different wastewaters were spiked and analyzed. The relative standard deviations of the percent recovery of these measurements are also included in Table 2.

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TABLE 1. CHROMATOGRAPHIC CONDITIONS AND ESTIMATED METHOD DETECTION LIMITS

Parameter	Retention Time (min.) Column 1	Retention Time (min.) Column 2	MDL (µg/L)
Chloropicrin	5.60	2.03	0.8
Ethylene Dibromide	9.90	3.15	0.2

Column 1 conditions: Carbopak B (60/80 mesh) coated with 1% SP-1000 packed in a 1.8 m long x 2 mm ID glass column with nitrogen carrier gas at a flow rate of 30 mL/min. Column temperature, isothermal at 135°C. An electron capture detector was used with this column to determine the MDL.

Column 2 conditions: Gas Chrom Q (100/120 mesh) coated with 30% OV-17 packed in a 1.8 m long by 2 mm ID glass column with helium carrier gas at a flow rate of 25 mL/min. Column temperature, isothermal at 95°C.

TABLE 2. SINGLE LABORATORY ACCURACY AND PRECISION[a]

Parameter	Sample Type[b]	Background µg/L[c]	Spike Level µg/L	Mean Recovery (%)	Standard Deviation (%)	Number of Replicates
Chloropicrin	1	ND	5	98	12	7
	2	ND	50	98	3.3	7
Ethylene Dibromide	1	ND	5	69	6.9	7
	2	ND	50	108	4.8	7

(a) Column 1 conditions were used.

(b) 1 = Low background relevant industrial effluent.
2 = High background relevant industrial effluent.

(c) ND = Not detected.

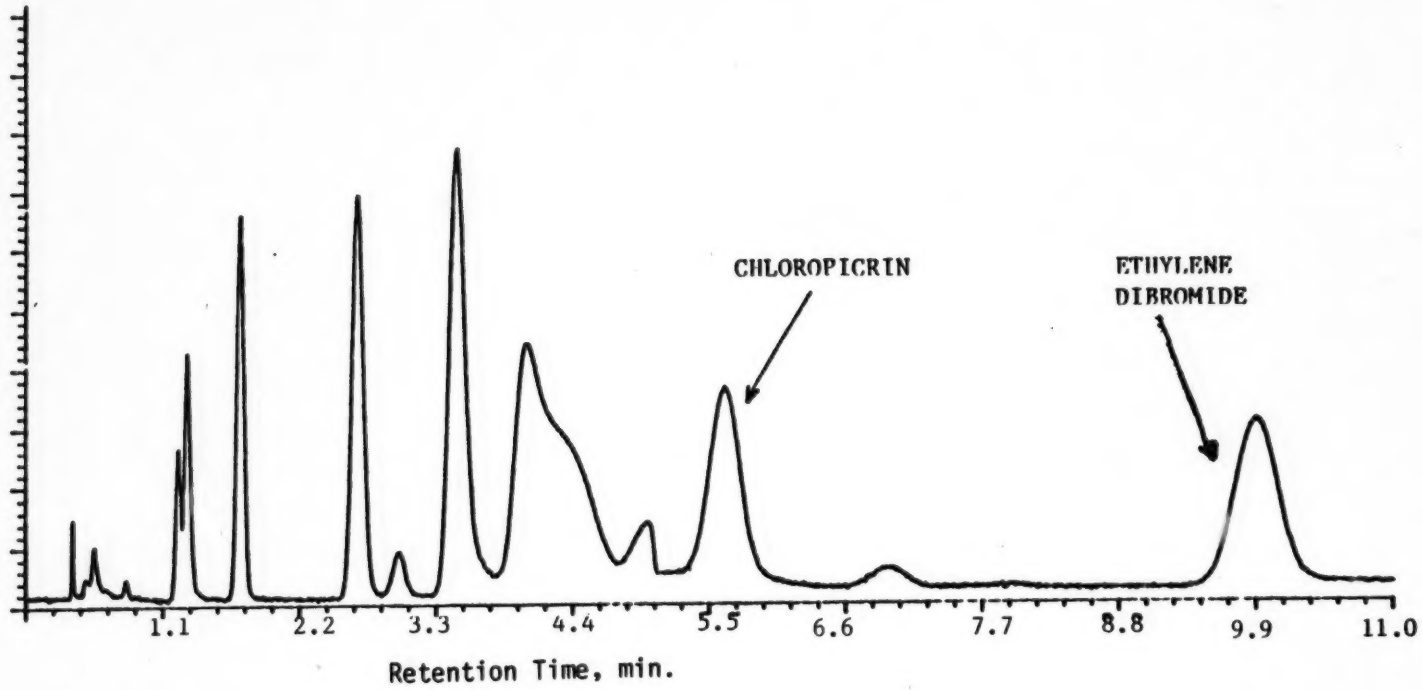

FIGURE 1. GC-ECD CHROMATOGRAM OF 200 ng CHLOROPICRIN AND ETHYLENE DIBROMIDE IN CYCLOHEXANE (COLUMN 1)

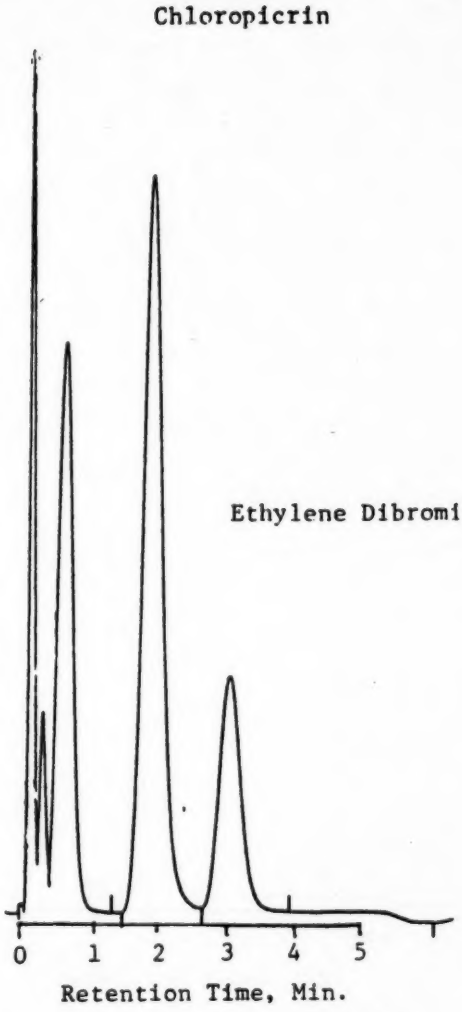

FIGURE 2. GC-ECD CHROMATOGRAM OF 400 ng CHLOROPICRIN AND ETHYLENE DIBROMIDE IN CYCLOHEXANE (COLUMN 2).